

**Subsolidus Phase Equilibria and Crystal Chemistry
in the System BaO-TiO₂-Ta₂O₅**

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Abstract

Subsolidus phase relations have been determined for the BaO:TiO₂:Ta₂O₅ system by X-ray diffraction analysis of ~100 specimens prepared in air at temperatures near but below the solidus (1275°C to 1500°C). For the BaO:Ta₂O₅ subsystem, the formation of all three polymorphs of BaTa₂O₆ (orthorhombic, tetragonal, and hexagonal) was confirmed. The present study found no stable phases forming between Ba₅Ta₄O₁₅ and BaO. In the ternary system, along the line BaTiO₃–Ba₅Ta₄O₁₅, the previously reported *8L* and *10L* hexagonal perovskite derivatives were confirmed, albeit with somewhat wider homogeneity ranges; BaTiO₃ dissolves Ta⁵⁺ up to BaTi_{0.64}Ta_{0.29}O₃, which contains 7% B-cation vacancies and exhibits a dilated cubic unit cell (*a*=4.0505(2) Å). The formation of Ba₃Ti₄Ta₄O₂₁, a member of the hexagonal A₃M₈O₂₁-type ternary oxides, was confirmed as well as its solid solution, for which a different mechanism of formation is suggested. Several new compounds have been found, including four members of the orthorhombic (space group *Cmcm*) “rutile-slab” homologous series, BaTi_nTa₄O_{11+2n}, with *n*-values 3,5,7,9; the unit cells for these compounds are given. Three ternary phases with close-packed [Ba,O] layer structures related to that of *6L* Ba₄Ti₁₃O₃₀ were found: *13L* Ba₁₈Ti₅₃Ta₂O₁₂₉, *7L* Ba₁₀Ti₂₇Ta₂O₆₉, and *8L* Ba₆Ti₁₄Ta₂O₃₉. The crystal structures of the *13L* and *7L* phases were determined by single-crystal X-ray diffraction (***13L* Ba₁₈Ti₅₃Ta₂O₁₂₉**: *cchcchcchcchc*, *C2/m*, *a*=9.859(2) Å, *b*=17.067(5) Å, *c*=30.618(8) Å, β=96.11(2)°, *Z*=2; ***7L* Ba₁₀Ti₂₇Ta₂O₆₉**: *cchcchc*, *C2/m*, *a*=9.855(3) Å, *b*=17.081(7) Å, *c*=16.719(7) Å, β=101.18(3)°, *Z*=2), and are described and compared with those of the *6L* and *8L* members of this family. Phases with tetragonal tungsten bronze (TTB) related structures occur over large compositional ranges in the BaO:TiO₂:Ta₂O₅ system, both within the ternary (Ba_{6-x}Ti_{2-2x}Ta_{8+2x}O₃₀, *x*=0→0.723), and along the BaO-Ta₂O₅ binary (from 43 to 26 mol% BaO), which in turn dissolves up to ~12 mol% TiO₂ to form extensive single-phase fields with different TTB superstructures. X-ray powder diffraction data are given for three binary BaO:Ta₂O₅ compounds exhibiting the TTB structure and two superstructures. The large compositional ranges of the TTB-type phases are accompanied by only small changes in specific volume. The TTB-type regions within the ternary and those emanating from the BaO-Ta₂O₅ binary do not co-exist in equilibrium, which likely reflects fundamental differences in the structural mechanisms that accommodate the variable stoichiometries. The similarities and differences between the BaO:TiO₂:Ta₂O₅ and BaO:TiO₂:Nb₂O₅ systems are described.

Keywords:

BaO:TiO₂:Ta₂O₅, BaO:Ta₂O₅, barium titanium tantalates, tetragonal tungsten bronze, BaTi_{0.64}Ta_{0.29}O₃, Ba₃Ti₄Ta₄O₂₁, BaTi_nTa₄O_{11+2n}, Ba₁₈Ti₅₃Ta₂O₁₂₉, Ba₁₀Ti₂₇Ta₂O₆₉, Ba₆Ti₁₄Ta₂O₃₉.

Introduction

Complex titanates, tantalates, and niobates display important dielectric properties that are exploitable, for example, in wireless communications applications [1-5]. As part of a continuing program to elucidate phase relations, crystal chemistry, and the occurrence of new compounds in this class of ceramic oxides, the first systematic study of the BaO-TiO₂-Ta₂O₅ system has been carried out and is described here.

Review of Previous Work

Studies of the phase equilibrium relationships of the TiO₂-Ta₂O₅ system [6-8] indicate that TiO₂ dissolves up to ~10 mol% Ta₂O₅, and that the compound TiTa₂O₇ forms with a structure analogous to that of TiNb₂O₇. In this arrangement, the metal ions are disordered in vertex-sharing octahedra arranged in blocks of the ReO₃ structure interlinked by edge-sharing [9,10]. At temperatures above ~1200°C, a solid solution of the high-temperature form of Ta₂O₅ forms with up to 10-15 mol% TiO₂.

The BaO-TiO₂ subsystem has been well studied [8,11-17]. At temperatures above 1200°C, four compounds referred to as barium polytitanates occur between TiO₂ and the well-known BaTiO₃; namely, Ba₂Ti₉O₂₀, BaTi₄O₉, Ba₄Ti₁₃O₃₀, and Ba₆Ti₁₇O₄₀. The first two compounds are technically important in dielectric resonator ceramics [4,5]. The crystal chemistry of the barium polytitanate phases has been described in considerable detail [18,19]. With the exception of BaTi₄O₉, which adopts a framework-type structure built from zig-zag chains of edge-sharing [TiO₆] octahedra, the polytitanate phases exhibit close-packed [Ba,O] layer structures with Ti occupying octahedral interstices. Between perovskite-type BaTiO₃ and BaO, the compound Ba₂TiO₄ forms with a β-K₂SO₄-type structure containing discrete tetrahedral [TiO₄] units [20].

A single report is available describing a systematic study of phase relations in the BaO-Ta₂O₅ system [8,21]. Six binary phases were reported to form at 6:1, 4:1, 3:1, 5:2, 1:1, and 1:2 BaO:Ta₂O₅ molar ratios. The three latter compounds are well-established: Ba₅Ta₄O₁₅ [22] is isostructural with Ba₅Nb₄O₁₅ and exhibits a five-layer hexagonal structure derived from perovskite. BaTa₂O₆ exhibits three polymorphs [23,24]: a low-temperature orthorhombic form

isostructural with BaNb_2O_6 , an intermediate form with a tetragonal tungsten bronze type structure, and a high temperature hexagonal form; all of the structures are of the framework type with octahedrally coordinated Ta^{5+} and channels accommodating barium. $\text{BaTa}_4\text{O}_{11}$ occurs with a tetragonal tungsten bronze related structure [25]. The occurrence and crystal chemistry of the higher-BaO compounds at 3:1, 4:1, and 6:1 $\text{BaO}:\text{Ta}_2\text{O}_5$ have not been well established; however, $\text{Ba}_4\text{Ta}_2\text{O}_9$ has been reported to exist in polymorphic forms with perovskite-related structures [26,27].

Although phase equilibria relations in the $\text{BaO}:\text{TiO}_2:\text{Ta}_2\text{O}_5$ have not been reported, several ternary compounds have been documented. These include 8-layer (8L) $\text{Ba}_8\text{Ti}_3\text{Ta}_4\text{O}_{24}$ [28,29] and 10L $\text{Ba}_{10}\text{Ta}_{7.04}\text{Ti}_{1.2}\text{O}_{30}$ [29], both of which are hexagonal perovskite derivatives that form as solid solutions along the composition line between BaTiO_3 and 5L hexagonal $\text{Ba}_5\text{Ta}_4\text{O}_{15}$. In addition, the solid solution $\text{Ba}_3\text{Ti}_{4+5x}\text{Ta}_{4-4x}\text{O}_{21}$ with $0 \leq x \leq 0.3$ [30] was reported as a member of the family of hexagonal framework-type $\text{A}_3\text{M}_8\text{O}_{21}$ ternary oxides [31-33], which share some structural similarities with the tetragonal and hexagonal bronzes [30].

Experimental Methods

Approximately 100 polycrystalline specimens (3-4 g each) were prepared by solid-state reaction of BaCO_3 (99.99% or 99.999%), TiO_2 (phosphate-free), and Ta_2O_5 (optical grade). Prior to each heat treatment, samples were ground with an agate mortar and pestle for 15 min, pelletized, and placed on sacrificial powder of the same composition in a Pt-foil-lined alumina combustion boat. After an initial overnight calcine at 950°C , multiple 2-5 d heatings (with intermediate grinding and re-pelletizing) were carried out at temperatures below but near the solidus, ranging from 1275 to 1500°C . Samples were furnace-cooled to $\sim 700^\circ\text{C}$ and then air-quenched on the bench-top. Typically, four to seven heatings were required to attain equilibrium, which was presumed when no further changes could be detected in the weakest peaks observed in the X-ray powder diffraction patterns. Reaction temperatures for the various compositions were chosen by considering the results of melting point experiments, and qualitative extrapolation of the reported solidus temperatures along the three binaries into the ternary system. The minimum solidus tem-

peratures observed in the ternary system were $\sim 1300^\circ\text{C}$, near the barium polytitanates ($\sim 30:64:6$ BaO:TiO₂:Ta₂O₅). Crystals of Ba₁₀Ti₂₇Ta₂O₆₉ and Ba₁₈Ti₅₃Ta₂O₁₂₉ were grown from slightly off-stoichiometric partial melts (25.64:71.80:2.56 BaO:TiO₂:Ta₂O₅ and 24.66:73.97:1.37 BaO:TiO₂:Ta₂O₅, respectively) in open platinum capsules (2.6 mm i.d.) that were soaked at 1450°C for 24 h, cooled at $3^\circ\text{C}/\text{h}$ to 1325° , furnace-cooled to 700°C , and finally quenched on the bench-top. The crystals were colorless, transparent, birefringent in polarized light, and mostly prismatic fragments of random size rather than with specifiable crystal faces.

Phase assemblages were ascertained from X-ray powder diffraction data, which were obtained with a Philips¹ diffractometer equipped with incident Soller slits, theta-compensating slit and a graphite monochromator, and a scintillation detector. Samples were mounted in wellled glass slides. Patterns were collected at ambient temperatures using CuK α radiation with a 0.02° 2θ step size and a 2 s count time. Intensity data measured as relative peak heights above background of hand-picked peaks were obtained using the Siemens DIFFRAC5000 second derivative peak locate program. The observed 2θ line positions reported here have been corrected using SRM 660, LaB₆ [34] as an external calibrant. Lattice parameters were refined using the corrected powder diffraction data (2θ values, CuK $\alpha_1 = 1.540562 \text{ \AA}$) with the least-squares program CELLSVD [35]. Powder patterns were calculated using the GSAS package [36].

Single crystals of Ba₁₈Ti₅₃Ta₂O₁₂₉ and Ba₁₀Ti₂₇Ta₂O₆₉ were characterized by the precession camera method (Zr-filtered Mo K α radiation) to assess quality, space group, and approximate cell parameters. Single-crystal X-ray diffraction data were obtained with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo K α radiation. A Gaussian integration absorption correction was applied to all measured intensities. Calculations were carried out using the NRCVAX [37] suite of programs. The structure was solved using Patterson and Fourier methods. Transition metal sites were initially assumed to be randomly occupied by a mixture of Ta⁵⁺ and Ti⁴⁺. The contrast between Ta and Ti by X-ray diffraction is sufficient to allow direct refinement of relative occupancies assuming mixed-atom sites containing $x\text{Ti} + (1-x)\text{Ta}$. The

¹ Certain commercial equipment is identified in order to adequately specify the experimental procedure; recommendation or endorsement by the National Institute of Standards and Technology is not therein implied.

overall stoichiometries were then deduced by simultaneous consideration of the refined occupancies and charge-balance in the presence of pentavalent tantalum and tetravalent titanium.

Results and Discussion

The subsolidus phase equilibria relations found in the present study are presented in Figure 1. The results found in each region of the system will be discussed in the following sections.

1. Binary BaO:Ta₂O₅ System

a. Tetragonal Tungsten Bronze (TTB) Related Phases from 43 to 26 mol% BaO

Although TTB-type BaTa₄O₁₁ (33 mol% BaO) was previously reported as a line compound [21], the present study found an extensive solid solution in this region of the binary system. This solid solution is similar to that found in the BaO:Nb₂O₅ system [38], and again demonstrates the remarkable stability of tetragonal tungsten bronze related structures over a wide range of stoichiometry. In the region (Fig. 1) from 43 to 39 mol% BaO, no superstructure formation was observed and powder patterns could be indexed on the basis of tetragonal 12 Å x 4 Å TTB-type unit cells [39]. Although the formula for the solid solution in this region can be written with oxygen-deficiency as Ba_{5-y}Ta₁₀O_{30-y}, with 1.2 ≤ y ≤ 1.8, there is no logical crystal chemical model to account for the possible oxygen vacancies. Alternatively, and preferably, if one assumes that the strongly bonded octahedral framework (denoted in the following by square brackets) remains intact, the formula for the TTB-type solid solution from 43 to 39 mol% BaO can be expressed as Ba_xTa_{(10-2x)/5}[Ta₁₀O₃₀], with x=3.93 to 3.40. In this model, Ba and the excess Ta occupy disordered sites within the channels, with Ta⁵⁺ lowering its coordination number by moving from the centers of the channels.

In the region from 38 to 31 mol% BaO, superstructures formed with *a*- and *b*-parameters related to those of the TTB structure by a factor of $\sqrt{2}$, yielding tetragonal or orthorhombic supercells similar to those observed in a number of other systems [40,41]. If one assumes that the formation of a supercell with a doubled unit-cell volume is caused by the ordering of 2 [TaO]

units per supercell in sites within the pentagonal channels, in a manner analogous to the formation of tripled superstructures in TTB-related $\text{Nb}_8\text{W}_9\text{O}_{47}$ [42,38], $\text{Sr}_2\text{Nb}_{10}\text{O}_{27}$, and $\text{SrTa}_4\text{O}_{11}$ [43], then a possible general formula for the $\sqrt{2}$ -type solid solution from 38 to 31 mol% BaO is $\text{Ba}_x\text{Ta}_{(14-2x)/5}[\text{Ta}_{22}\text{O}_{62}]$, with $x = 6.77$ to 5.11 , respectively. This model would not require the formation of oxygen vacancies; Ba and excess Ta not associated with the framework would occupy disordered sites within the channels.

In the region from 30 to 26 mol% BaO, tripling of the TTB b -parameter was observed, resulting in a unit cell with a tripled cell volume. As in $\text{Nb}_8\text{W}_9\text{O}_{47}$ [42,38], the formula for the framework of the tripled TTB structure is $[\text{M}_{34}\text{O}_{94}]$, which includes the 4 [MO] units occupying ordered pentagonal channel sites. Therefore, a possible general formula for the tripled-cell-type solid solution from 30 to 26 mol% BaO is $\text{Ba}_x\text{Ta}_{(18-2x)/5}[\text{Ta}_{34}\text{O}_{94}]$, with $x = 7.42$ to 6.17 , respectively. As above, this model does not require the formation of oxygen vacancies, and Ba and excess Ta not associated with the $[\text{M}_{34}\text{O}_{94}]$ framework would occupy disordered sites within the channels. Detailed structural determinations have not yet been carried out to confirm these suggested mechanisms accommodating the variable stoichiometry and leading to the formation of the different superstructures.

Tables 1-4 give refined unit cells and indexed powder diffraction data for binary compounds in each of the TTB-type solid solution regions. Interestingly, as seen in Table 1, and as also observed in the BaO- Nb_2O_5 system [38], the TTB-type framework maintains a nearly constant specific volume, within $\sim 0.5\%$, despite the large range in BaO-content. As seen in Fig. 1, the three TTB-type regions extend into the ternary system, dissolving up to ~ 12 mol% TiO_2 . The superstructures are preserved upon substitution of Ti, with slight ($\sim 1\%$) but systematic increases in unit cell volumes.

b. BaTa₂O₆

The polymorphism of BaTa_2O_6 has been described by Layden [23,24]. Below about 1150°C a modification isostructural with orthorhombic BaNb_2O_6 forms, between $\sim 1150^\circ\text{C}$ and 1300°C a tetragonal tungsten bronze type structure forms, and above 1300°C a hexagonal modification oc-

curs. For the latter form, a structural model was proposed that was consistent with X-ray powder diffraction data ($P6/mmm$; $a=21.14 \text{ \AA}$, $c=3.917 \text{ \AA}$; $Z=12$) [24]. In the BaO-Nb₂O₅ system, the same hexagonal structure was found to form at the composition Ba_{0.9}Nb₂O_{5.9} [38]. In the present work, single crystals of all three forms of BaTa₂O₆ were obtained using a BaO:V₂O₅ flux. Complete structural refinements are in progress for the tetragonal and hexagonal polymorphs and will be described elsewhere. Preliminary results indicate that: 1) for the hexagonal structure, one of the Ba sites originally placed at $z=0$ [24] is actually at $z=0.28$, changing the coordination number from an unlikely 18 to a more reasonable 12; and 2) the tetragonal form crystallizes in the non-polar space group $P4b2$ rather than the more commonly found $P4bm$ [44].

Mixtures prepared along the BaTa₂O₆-Ba₅Ta₄O₁₅ join and annealed at temperatures above 1300°C (e.g. 1550°C) were found to contain the tetragonal tungsten bronze type form of BaTa₂O₆, indicating that this polymorph is kinetically stabilized in this region.

c. Between Ba₅Ta₄O₁₅ and BaO

The X-ray powder diffraction patterns of specimens in this region, prepared by either slow-cooling or quenching, were not reproducible, most likely because of reaction with moisture and/or CO₂. No evidence of the formation of the compounds Ba₆Ta₂O₁₁ or Ba₃Ta₂O₈ [21] was observed. Although some specimens contained a hexagonal phase with a unit cell ($a=5.926 \text{ \AA}$, $c=4.234 \text{ \AA}$) analogous to that reported for Ba₄Ta₂O₉ [21,26,27], in the present study this phase was found to decompose upon further heat treatment at 1100°C.

1. Ternary BaO:TiO₂:Ta₂O₅ System

a. The Rutile-Slab Series, BaTi_nTa₄O_{11+2n}, $n=3,5,7,9$

A new family of compounds BaTi₃Ta₄O₁₇, BaTi₅Ta₄O₂₁, BaTi₇Ta₄O₂₅, and BaTi₉Ta₄O₂₉ was observed to form in the BaO:TiO₂:Ta₂O₅ system. According to X-ray powder diffraction data, these phases are isostructural with the orthorhombic “chemically twinned rutile” homologous series observed in the (K,Na)₂O:TiO₂:(Nb,Ta)₂O₅ [45,46], BaO:TiO₂:Nb₂O₅ [47], and

SrO:TiO₂:Nb₂O₅ [48] systems. The structures, crystallizing in space group *Cmcm*, feature slabs of the rutile structure joined together by vertex-sharing [MO₆] octahedra such that pseudo-hexagonal tunnels are formed for the larger 7-coordinated A-cations [48]. Adjacent rutile slabs are related by a mirror plane containing the alkali or alkaline-earth cation, hence the designation “chemically twinned rutile”. Successive members of the series are generated by adding 2TiO₂ to the width of the rutile slabs, thus increasing the *c*-axis by ~4.4 Å per member, whereas the *a*- and *b*-axes remain relatively constant. The refined unit cell parameters for the n=3,5,7, and 9 members that form in the BaO:TiO₂:Ta₂O₅ system are given in Table 5. Members with n-values larger than 9 may also form, as they do in the SrO:TiO₂:Nb₂O₅ system [48], but were not investigated in the present study.

b. Ba₃Ti₄Ta₄O₂₁ Solid Solution

This phase belongs to the family of hexagonal A₃M₈O₂₁ ternary oxides initially described by Groult, et al. [31,32], with Ba or K as the A-cation, and Nb as the M-cation which in turn could be partially substituted by a variety of metals including Ti, Cr, Fe, Ni, Mg, and Zn (*P6₃/mcm*; *a* ~ 9 Å, *c* ~ 12 Å; Z=2). The framework-type structure is built from [MO₆] octahedra sharing vertices and edges, and shares similarities with the tetragonal tungsten bronze arrangement [30]. The compound Ba₃LiM₃Ti₅O₂₁ (M=Nb,Ta,Sb) was also reported to form with the A₃M₈O₂₁-type structure [49], and it was suggested that the extra Li cations were accommodated in interstitial sites in the framework. The same mechanism was suggested for the A₃M₈O₂₁-type solid solutions Ba₃M_{4-4x}Ti_{4+5x}O₂₁ (M=Nb,Ta) with 0 ≤ x ≤ 0.3 [30,33], which were studied by Rietveld analysis using X-ray powder diffraction data. For this series the total B-cation count is 8+x. The authors state that the extra Nb/Ta (=x) beyond the 8 needed to form the octahedral framework occupy tricapped trigonal prismatic sites formed by [M₆O₂₄] units of 2x3 edge- and corner-sharing octahedra. According to this study then the structure forms for compositions Ba₃Ti₄Ta₄O₂₁ (=3:4:2) through Ba₃Ti_{5.5}Ta_{2.5}(Ta_{0.3})O₂₁ (=3:5.5:1.4), with 0.3 Ta in 9-coordinated tricapped trigonal prismatic (Wyckoff 2a) sites. A similar solid-solution limit was reported for the analogous system with Nb instead of Ta in a study of the BaO–TiO₂–Nb₂O₅ phase diagram [47].

In the present study of the BaO–TiO₂–Ta₂O₅ system, the A₃M₈O₂₁-type phase exhibited a hexagonal unit cell in agreement with the previous work [30]; with increasing x-value, the *a*-parameter decreases slightly while the opposite trend is observed for the *c*-parameter, resulting in a nearly constant unit cell volume for the solid solution. However, the Ba₃Ti_{4+5x}Ta_{4-4x}O₂₁ specimen with x=0.3 contained traces of secondary phases. X-ray diffraction studies are in progress of single crystals of the solid solution grown from an off-stoichiometric (6:14:1 BaO:TiO₂:Ta₂O₅) melt. Preliminary refinement results have confirmed the expected space group and unit cell (*P6₃/mcm*; *a* ~ 9.99 Å, *c* ~ 11.85 Å), with metal occupancies yielding the stoichiometry Ba₃Ta_{2.70(3)}Ti_{5.30(3)}O_{20.35}; however, no electron density was observed in the tri-capped trigonal prismatic (Wyckoff 2a) sites. The extra cations are likely located elsewhere. However, an alternative mechanism for the solid solution might be the formation of oxygen vacancies; i.e., Ba₃Ti_{4+y}Ta_{4-y}O_{21-y/2}, with 0 ≤ y ≤ 1.3. This possible alternative formula would shift the line along which the solid solution forms to slightly higher Ba content, as shown in Fig. 1 and 2, with the end-member occurring at 3:5.3:1.35 BaO:TiO₂:Ta₂O₅ instead of 3:5.5:1.4, as reported previously [30]. Further structural analysis is needed and will be reported elsewhere.

c. The Ba₄Ti₁₃O₃₀ Structural Family: Ba₁₈Ti₅₃Ta₂O₁₂₉, Ba₁₀Ti₂₇Ta₂O₆₉, and Ba₆Ti₁₄Ta₂O₃₉

The compounds forming in this region of the phase diagram are structurally similar to those found in analogous regions of the BaO:TiO₂:Nb₂O₅ system [50], and form on a line between Ba₄Ti₁₃O₃₀ and Ba₆Ti₁₄Ta₂O₃₉, as shown in Fig. 2. All of the phases exhibit structures built from similar close-packed (*cp*) [O,Ba] layers, with octahedral interstices occupied by Ti/Ta. As found in the barium polytitanates [19] and other [O,Ba] layer structures [51], the *cp* layers are distorted and defective wherein some of the Ba ions occur in pairs which substitute for three oxygens in a row, thus leaving a vacant *cp* site between them, and lowering the Ba coordination number from 12 to 11. The Ba pairs occur in regular patterns that result in two types of polyhedral layers, one with strings of three distorted edge-sharing [(Ti/Ta)O₆] octahedra, and another with groups of five similarly distorted edge-sharing [(Ti/Ta)O₆] octahedra. The structures of Ba₄Ti₁₃O₃₀, Ba₁₈Ti₅₃Ta₂O₁₂₉, Ba₁₀Ti₂₇Ta₂O₆₉, and Ba₆Ti₁₄Ta₂O₃₉ are all built from these two types of layers, which are illustrated in Fig. 3 for six-layer (*6L*) Ba₄Ti₁₃O₃₀ [53,12]. The stacking sequence of

the *cp* layers in $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ is $(chc)_2$, and results in an orthorhombic structure (*Cmca*; $a=17.063$ Å, $b=9.864$ Å, $c=14.053$ Å; $Z=4$) [53].

Although the compounds $\text{Ba}_{18}\text{Ti}_{53}\text{Ta}_2\text{O}_{129}$ and $\text{Ba}_{10}\text{Ti}_{27}\text{Ta}_2\text{O}_{69}$ were difficult to purify in polycrystalline form, single crystals were readily grown from off-stoichiometric partial melts. The details of the single-crystal X-ray diffraction studies of these two phases are given in Table 6. The refined structural parameters for $\text{Ba}_{18}\text{Ti}_{53}\text{Ta}_2\text{O}_{129}$ are given in Table 7. This compound crystallizes with a monoclinic *13L* structure having the stacking sequence *cchcchcchcchc*; the thirteen polyhedral layers are illustrated in Fig. 4 and are seen to consist of the same two types as in *6L* $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ (Fig. 3). Oxygen vacancies in the *cp* layers that occur between pairs of Ba ions lower the coordination numbers of Ba 1, Ba 4, and Ba 5 from 12 to 11. The Ti/Ta octahedra are somewhat distorted, with bond distances ranging from 1.780 Å to 2.160 Å. $\text{Ba}_{18}\text{Ti}_{53}\text{Ta}_2\text{O}_{129}$ is most likely isostructural with the *13L* monoclinic phase reported earlier [50] with a similar unit cell, and with the approximate composition $\text{Ba}_{18}\text{Ti}_{54}\text{Nb}_2\text{O}_{131}$, as derived from structural principles and X-ray powder diffraction data [50].

$\text{Ba}_{10}\text{Ti}_{27}\text{Ta}_2\text{O}_{69}$ crystallizes with a monoclinic *7L* structure having the stacking sequence *cchcchc*; the refined structural parameters are given in Table 8. The seven polyhedral layers are illustrated in Fig. 5, and consist of the same two types as in *6L* $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ (Fig. 3) and *13L* $\text{Ba}_{18}\text{Ti}_{53}\text{Ta}_2\text{O}_{129}$ (Fig. 4). Oxygen vacancies in the *cp* layers between pairs of Ba ions lower the coordination numbers of Ba 1 and Ba 3 from 12 to 11. Similar to $\text{Ba}_{18}\text{Ti}_{53}\text{Ta}_2\text{O}_{129}$, the Ti/Ta octahedra are somewhat distorted, with bond distances ranging from 1.741 Å to 2.146 Å. $\text{Ba}_{10}\text{Ti}_{27}\text{Ta}_2\text{O}_{69}$ is most likely isostructural with the *7L* monoclinic phase found in the $\text{BaO}:\text{TiO}_2:\text{Nb}_2\text{O}_5$ system [50] with a similar unit cell, and reported to occur with the approximate formula $\text{Ba}_{10}\text{Ti}_{28}\text{Nb}_2\text{O}_{71}$, which was derived from structural principles and X-ray powder diffraction data. The formulas for both the *7L* and *13L* phases were overestimated by one TiO_2 in the earlier study [50].

Single crystals of $\text{Ba}_6\text{Ti}_{14}\text{Ta}_2\text{O}_{39}$ were also obtained, and the results of a complete structural determination of this phase, as well as the previously reported Nb-analog $\text{Ba}_6\text{Ti}_{14}\text{Nb}_2\text{O}_{39}$, [50] will be described elsewhere. $\text{Ba}_6\text{Ti}_{14}\text{Ta}_2\text{O}_{39}$ crystallizes with an orthorhombic *8L* structure hav-

ing the stacking sequence $(hccc)_2$ ($Cmca$; $a \sim 17.1$ Å, $b \sim 9.86$ Å, $c \sim 18.7$ Å; $Z=4$). The preliminary refinement results for the Nb-analog were used to illustrate the eight polyhedral layers shown in Fig. 6. Once again the layers are seen to consist of the same two types (layers with strings of three edge-sharing octahedra and layers with groups of five edge-sharing octahedra) as for $6L$ $Ba_4Ti_{13}O_{30}$ (Fig. 3), $13L$ $Ba_{18}Ti_{53}Ta_2O_{129}$ (Fig 4), and $7L$ $Ba_{10}Ti_{27}Ta_2O_{69}$ (Fig. 5).

The structures of all four members of the $Ba_4Ti_{13}O_{30}$ family are illustrated in Fig. 7, viewed parallel to the cp layers with the stacking direction vertical in the page. The a - and b - unit cell dimensions are similar for all four phases, with the c -dimensions reflecting the number of layers, which exhibit a common thickness of 2.34 Å per layer.

d. Tetragonal Tungsten Bronze (TTB) Type Solid Solution $Ba_{6-x}Ti_{2-2x}Ta_{8+2x}O_{30}$

As shown in Fig. 1, this solid solution forms along the line $Ba_6Ti_2Ta_8O_{30}$ – $BaTa_2O_6$, with a maximum x -value of 0.723. No evidence of superstructure formation was observed, and all observed lines in the X-ray powder diffraction patterns could be indexed with TTB-type [39] unit cells (Table 9). The $x=0$ endmember $Ba_6Ti_2Ta_8O_{30}$ forms at the ideal $A_6B_{10}O_{30}$ TTB stoichiometry, with all sites fully occupied. The solid solution forms by the coupled formation of Ba-site vacancies and substitution of Ta^{5+} for Ti^{4+} . As seen in Table 9, the unit cell volume decreases by only ~0.15% despite removal of 12 % of the Ba ions at the solid solution limit of $x=0.723$. Interestingly, despite strong similarities in crystal chemistry, no tie lines were found between this TTB solid solution and the extensive TTB-related phase fields occurring along the binary BaO - Ta_2O_5 system (Fig 1). The observation that these regions do not occur in equilibrium with each other may reflect fundamentally different structural mechanisms of solid-solution formation: whereas the $Ba_{6-x}Ti_{2-2x}Ta_{8+2x}O_{30}$ phases form by straightforward depletion of A-sites, the extensive TTB solid solutions along the binary, as discussed above, require a more complex mechanism with Ta probably occupying channel sites.

e. The Quasi-binary system Ba₅Ta₄O₁₅–BaTiO₃

The crystal chemistry that arises when BaTiO₃ is added to Ba₅Ta₄O₁₅ features close-packed layer structures derived from perovskite by introducing B-cation vacancies and variable layer sequencing. Five-layer (*5L*) Ba₅Ta₄O₁₅ (*P3m1*; *a*=5.776 Å, *c*=11.82 Å; *Z*=1; packing sequence *cchhc*) [22] is isostructural with Ba₅Nb₄O₁₅ [38] (and also Sr₅Nb₄O₁₅), and is the *n*=5 member of the “perovskite-slab” series A_{*n*}B_{*n*-1}O_{3*n*}. These structures feature ordered layers of B-cation vacancies separating slabs of the perovskite structure that are four (= *n*-1) [BO₆] octahedra in thickness. The slabs extend parallel to the parent (111) perovskite planes, resulting in the tendency of the structures to crystallize with hexagonal symmetry. In the BaO:TiO₂:Nb₂O₅ system, the *n*=6 and *n*=8 members form [47,28], and in the SrO:TiO₂:Nb₂O₅ systems, the *n*=6 [54] and *n*=7 members form. Compounds in this series can form broad solid solutions for reasons which have not been fully explained by detailed structural investigations, but which most likely include both variations in vacancy-ordering (or disordering) as well as the formation of random and ordered intergrowths of different members of the series.

In the BaO:TiO₂:Ta₂O₅ system an 8-layer (Ba₈Ti₃Ta₄O₂₄) [28,29] and a 10-layer (Ba₁₀Ta_{7.04}Ti_{1.2}O₃₀) [29] phase have been reported to occur along the Ba₅Ta₄O₁₅–BaTiO₃ line. A study of polycrystalline samples using X-ray diffraction and high resolution electron microscopy [29] produced structural models for both which indicated that these two phases are not members of the perovskite-slab A_{*n*}B_{*n*-1}O_{3*n*} series, in contrast to the BaO:TiO₂:Nb₂O₅ and SrO:TiO₂:Nb₂O₅ systems. Ba₈Ti₃Ta₄O₂₄ exhibited superstructure formation within the close-packed [BaO₃] layers, which were stacked with an *8L* (*cchc*)₂ sequence (*P6₃/mcm*; *a*=10.0314 Å, *c*=18.869 Å; *Z*=3). Ba₁₀Ta_{7.04}Ti_{1.2}O₃₀ exhibited a *10L* (*cchcc*)₂ close-packed layer sequence with some disorder (*P6₃/mmc*; *a*=5.7981 Å, *c*=23.755 Å; *Z*=1). The suggested structural models do not feature slabs of the perovskite structure as in the A_{*n*}B_{*n*-1}O_{3*n*} series; rather, the B-cation vacancies are distributed throughout the layers, resulting in a fully three-dimensional arrangement. Both the *8L* and *10L* phases were reported to exhibit wide stoichiometric ranges.

In the present study both of the previously reported *8L* and *10L* phases were confirmed; the unit cells and observed X-ray powder diffraction patterns were similar to those calculated from

the data provided in the earlier work [29]. Somewhat different homogeneity ranges were obtained, which likely results from differences in sample preparation temperatures. Using the notation $(1-x)\text{Ba}_5\text{Ta}_4\text{O}_{15}:x\text{BaTiO}_3$, the *10L* phase was observed here to form in the region $x = 0.20 \rightarrow 0.40$, as compared with $x = 0.24 \rightarrow 0.40$ indicated by the previously reported range of homogeneity [29]. In agreement with the earlier work [29], the cell parameters decrease with increasing Ti content or x -value. The *8L* phase was observed here to form in the range $x = 0.50 \rightarrow 0.80$ (note that the ideal composition $\text{Ba}_8\text{Ti}_3\text{Ta}_4\text{O}_{24}$ occurs at $x=0.75$), as compared to $x = 0.66 \rightarrow 0.75$ reported previously [29]; as for the *10L* phase, increasing Ti content or x -value causes a decrease in unit cell volume, in agreement with the earlier work [29]. Another solid solution from the end-member $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ ($x=0$) to $x=0.15$, as shown in Fig. 1, was observed in the present study; however, the X-ray powder diffraction patterns of specimens in this region suggest that they may be complex intergrowths rather than true solid solutions, as found similarly in the $\text{BaO}:\text{TiO}_2:\text{Nb}_2\text{O}_5$ system [47].

BaTiO₃-type solid solution: From $x=0.90$ to $x=1$, $(1-x)\text{Ba}_5\text{Ta}_4\text{O}_{15}:x\text{BaTiO}_3$, a cubic perovskite-type solid solution occurs. As found in the $\text{BaO}:\text{TiO}_2:\text{Nb}_2\text{O}_5$ [47] and $\text{SrO}:\text{TiO}_2:\text{Nb}_2\text{O}_5$ systems, the solid solution forms by introduction of B-cation vacancies (\square), according to the formula $\text{BaTi}_{1-y}\text{Ta}_{4y/5}\square_{y/5}\text{O}_3$. The observed solid-solution limit for a specimen prepared at 1550°C corresponds to $y=0.36$, or $\text{BaTi}_{0.64}\text{Ta}_{0.29}\text{O}_3$, with 7 % of the B-cation sites vacant. Introduction of Ta^{5+} plus vacancies causes the lattice to dilate, with the cubic unit cell parameter varying from $a \sim 4.016 \text{ \AA}$ near $y=0$ to $a=4.0505(2) \text{ \AA}$ at the limit of $y=0.36$.

f. High-BaO Region above the Line $\text{Ba}_5\text{Ta}_4\text{O}_{15}-\text{BaTiO}_3$

The X-ray powder diffraction patterns of specimens in this region indicated the presence of hydrated BaO, plus the phases found in the quasi-binary system $\text{Ba}_5\text{Ta}_4\text{O}_{15}-\text{BaTiO}_3$. None of the compounds previously reported to occur between $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ and BaO [21,26,27] were detected.

g. Comparison with the BaO:TiO₂:Nb₂O₅ system

Since Ta⁵⁺ and Nb⁵⁺ exhibit similar ionic radii [55] and crystal chemistries, similarities are expected between the BaO:TiO₂:Ta₂O₅ system and the Nb₂O₅ analog [47,50]. The rutile-slab compounds BaTi_n(Ta,Nb)₄O_{11+2n} are found in both systems, although the n=1 member forms in the Nb- but not the Ta-system. The monoclinic compound reported near the composition 3BaO:5TiO₂:3Nb₂O₅ [47] is not observed for Ta. In the Nb-system, analogs of the Ba₄Ti₁₃O₃₀ related phases – *13L* Ba₁₈Ti₅₃Ta₂O₁₂₉, *7L* Ba₁₀Ti₂₇Ta₂O₆₉, and *8L* Ba₆Ti₁₄Ta₂O₃₉ – are also found, but in addition a fourth, *20L* orthorhombic member forms between the *13L* and *7L* phases, with the approximate stoichiometry Ba₁₄Ti₄₀Nb₂O₉₉ [50]. For both systems, the A₃M₈O₂₁-type solid solution regions extending from Ba₃Ti₄(Nb,Ta)₄O₂₁ are essentially identical. The tetragonal tungsten bronze related phases are stable over considerably wider compositional ranges in the BaO:TiO₂:Ta₂O₅ system as compared to the Nb-system: the TTB regions along the BaO:Ta₂O₅ binary dissolve much more TiO₂, and the TTB solid solution within the ternary, Ba_{6-x}Ti_{2-2x}Ta_{8+2x}O₃₀, extends to higher x-values (0.72 vs. 0.5) [50]. Finally, the crystal-chemistry along the quasi-binary system Ba₅Ta₄O₁₅–BaTiO₃ is quite different from that found in the Nb-system: BaTiO₃ dissolves approximately three times more Ta⁵⁺ than Nb⁵⁺. From the end of the BaTiO₃ solid solution to Ba₅Ta₄O₁₅, the behavior is very different from the Nb-system, although all of the phases that form in both systems are apparently hexagonal: The Ta-system features an extensive solid solution of an *8L* phase, and two more solid solutions of a *10L* phase and the *5L* endmember Ba₅Ta₄O₁₅. In the Nb-system, an *8L* phase also forms with a limited range of solid solution (and, apparently, a different crystal structure than in the Ta system), and a *6L* phase occurs. The *6L* phase forms a “solid solution” to the endmember, *5L* Ba₅Nb₄O₁₅, which actually consists of a complex series of intergrowths of the *5L* and *6L* structures rather than a true solid solution.

Conclusions

Subsolidus phase relations have been determined for the BaO:TiO₂:Ta₂O₅ system in air. For the binary BaO:Ta₂O₅ subsystem, the formation of all three polymorphs of BaTa₂O₆ (orthorhombic, tetragonal, and hexagonal) was confirmed. The present study found no stable phases form-

ing between $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ and BaO . In the ternary system, along the line BaTiO_3 – $\text{Ba}_5\text{Ta}_4\text{O}_{15}$, the occurrence of the previously reported $8L$ and $10L$ perovskite derivatives was confirmed, albeit with somewhat wider homogeneity ranges; BaTiO_3 dissolves a considerable amount of Ta^{5+} by forming up to 7% B-cation vacancies. The formation of $\text{Ba}_3\text{Ti}_4\text{Ta}_4\text{O}_{21}$, a member of the hexagonal $\text{A}_3\text{M}_8\text{O}_{21}$ -type ternary oxides, was confirmed as well as its solid solution, for which a different mechanism of formation is suggested. Several new compounds have been found, including four members of the orthorhombic “rutile-slab” homologous series, $\text{BaTi}_n\text{Ta}_4\text{O}_{11+2n}$, with n -values 3,5,7,9. Three ternary phases with close-packed [Ba,O] layer structures related to that of $6L$ $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ were found: $13L$ $\text{Ba}_{18}\text{Ti}_{53}\text{Ta}_2\text{O}_{129}$, $7L$ $\text{Ba}_{10}\text{Ti}_{27}\text{Ta}_2\text{O}_{69}$, and $8L$ $\text{Ba}_6\text{Ti}_{14}\text{Ta}_2\text{O}_{39}$. The crystal structures of the $13L$ and $7L$ phases were determined by single-crystal X-ray diffraction, and are described and compared with those of the $6L$ and $8L$ members of this family as well as analogs found previously in the $\text{BaO}:\text{TiO}_2:\text{Nb}_2\text{O}_5$ system. Phases with tetragonal tungsten bronze related structures occur over large compositional ranges in the $\text{BaO}:\text{TiO}_2:\text{Ta}_2\text{O}_5$ system, both within the ternary ($\text{Ba}_{6-x}\text{Ti}_{2-2x}\text{Ta}_{8+2x}\text{O}_{30}$, $x=0\rightarrow 0.723$), and along the $\text{BaO}-\text{Ta}_2\text{O}_5$ binary (from 43 to 26 mol% BaO), which in turn dissolves up to ~12 mol% TiO_2 to form extensive single-phase fields. The TTB-type regions within the ternary and those emanating from the $\text{BaO}-\text{Ta}_2\text{O}_5$ binary do not co-exist in equilibrium, which likely reflects fundamental differences in the structural mechanisms that accommodate the variable stoichiometries. The similarities and differences between the closely related $\text{BaO}:\text{TiO}_2:\text{Ta}_2\text{O}_5$ and $\text{BaO}:\text{TiO}_2:\text{Nb}_2\text{O}_5$ systems have been described.

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Figure Captions

- Figure 1.** Subsolidus phase relations obtained for the BaO:TiO₂:Ta₂O₅ system from specimens prepared in air at 1275°C to 1500°C. Tetragonal tungsten bronze related phases occur along the BaO-Ta₂O₅ binary from 0.26 to 0.43 mol % BaO; the notations TTB, $\sqrt{2}$, and 3x refer to the superstructures observed (Table 1). Phases A→D are the “rutile-slab” homologous compounds, BaTi_nTa₄O_{11+2n}, with n-values 3,5,7,9, respectively. E = Ba₃Ti₄Ta₄O₂₁, with solid solution up to 3:5.3:1.35 BaO:TiO₂:Ta₂O₅. F = Ba₆Ti₁₄Ta₂O₃₉ (6:14:1), the 8L member of the Ba₄Ti₁₃O₃₀ family of ternary phases shown more clearly in Fig. 2. G = TTB-type Ba₆Ti₂Ta₈O₃₀, which forms the solid solution Ba_{6-x}Ti_{2-2x}Ta_{8+2x}O₃₀, x=0→0.723 H = hexagonal, defect perovskite 8L solid solution. I = hexagonal, defect perovskite 10L solid solution.
- Figure 2.** Expanded portion of the BaO:TiO₂:Ta₂O₅ diagram showing the Ba₄Ti₁₃O₃₀ (6L) family of ternary phases Ba₁₈Ti₅₃Ta₂O₁₂₉ (13L), Ba₁₀Ti₂₇Ta₂O₆₉ (7L), and Ba₆Ti₁₄Ta₂O₃₉ (8L, “6:14:1”=F).
- Figure 3.** Illustration [52] of the polyhedral layers in orthorhombic 6L Ba₄Ti₁₃O₂₀, cp layer stacking sequence (chc)₂ (Cmca; a=17.063 Å, b=9.864 Å, c=14.053 Å; Z=4) [53]. Spheres denote Ba²⁺; vertices of distorted [TiO₆] octahedra represent oxygens. The structure is built from two types of layers, one with strings of three edge-sharing octahedra (layers 1,4), the other with groups of five edge-sharing octahedra (layers 2,3,5,6).
- Figure 4.** Illustration of the polyhedral layers in 13L Ba₁₈Ti₅₃Ta₂O₁₂₉, cp layer stacking sequence cchcchcchcchc (C2/m; a=9.859(2) Å, b=17.067(5) Å, c=30.618(8) Å, β=96.11(2)°; Z=2). Spheres denote Ba²⁺; vertices of distorted [(Ti,Ta)O₆] octahedra represent oxygens. The structure is built from the same two types of layers as 6L Ba₄Ti₁₃O₂₀, as can be seen by comparison with Fig. 3.
- Figure 5.** Illustration of the polyhedral layers in 7L Ba₁₀Ti₂₇Ta₂O₆₉, cp layer stacking sequence cchcchc (C2/m; a=9.855(3) Å, b=17.081(7) Å, c=16.719(7) Å, β=101.18(3)°; Z=2). Spheres denote Ba²⁺; vertices of distorted [(Ti,Ta)O₆] octahedra represent oxygens. The structure is built from the same two types of layers as 6L Ba₄Ti₁₃O₂₀ and 13L Ba₁₈Ti₅₃Ta₂O₁₂₉, as can be seen by comparison with Figs. 3 and 4.
- Figure 6.** Illustration of the polyhedral layers in 8L Ba₆Ti₁₄Ta₂O₃₉, cp layer stacking sequence (hccc)₂ (Cmca; a~17.1 Å, b~9.86 Å, c~18.7 Å; Z=4), drawn using preliminary refinement results of isostructural Ba₆Ti₁₄Nb₂O₃₉. Spheres denote Ba²⁺; vertices of distorted [(Ti,Ta)O₆] octahedra represent oxygens. The structure is built from the

same two types of layers as $6L$ $Ba_4Ti_{13}O_{20}$, $13L$ $Ba_{18}Ti_{53}Ta_2O_{129}$, and $7L$ $Ba_{10}Ti_{27}Ta_2O_{69}$, as can be seen by comparison with Figs. 3, 4, and 5.

Fig 7 The structurally related series of compounds occurring along a line from $Ba_4Ti_{13}O_{20}$ to $Ba_6Ti_{14}Ta_2O_{39}$, viewed parallel to the cp layers along the ~ 17 Å unit cell axes (**a** or **b**). The layers are stacked along the c -axes which are vertical (or nearly so) in the page. Yellow spheres denote Ba^{2+} , red spheres denote oxygen, and distorted blue octahedra are occupied by Ti/Ta. For all four compounds, the average layer thickness is 2.34 Å. All the structures are built from the same two types of polyhedral layers, illustrated in Figs. 3-6.